ON THE RAMAN SPECTRA OF SOLUTIONS OF ORTHO-CHLOROPHENOL

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Plate V

ABSTRACT. The Raman spectra of 15% and 30% solutions of *o*-chlorophenol in carbon tetrachloride, chloroform and cyclohexane have been investigated and the relative intensity of the line 3533 cm^{-1} due to O–H valence oscillation has been measured with respect to that of the line 1416 cm^{-1}. It has been observed that the intensity of the line increases when the liquid is dissolved in the solvents and it increases further when the concentration is diminished from 30% to 15%. It has been concluded from these results that at a very low concentration the intensity of the line 3533 cm^{-1} is expected to increase still further. It has been pointed out that as this line is assigned to the O–H valence oscillation in the molecule with the O–H group in the trans position, such molecules become predominant in the solution at very low concentrations, and therefore, the strong infrared absorption peak at 6910 cm^{-1} observed in .01 molal solution in carbon tetrachloride cannot be ascribed to O–H vibration in the group in the cis position. It is suggested that the peak may be due to vibration in the O–H group in the trans position under the influence of surrounding carbon tetrachloride molecules. It has been suggested that infrared absorption band at 6610 cm^{-1} of the pure liquid might be due to a combination tone in the molecule of cis form.

INTRODUCTION

It was observed by previous workers that in the Raman spectra of both phenol and *o*-chlorophenol there is a weak line of Raman frequency about 3520 cm^{-1} (Kohlrausch and Pongratz, 1933, 1934). Wulf and Liddell (1935) on the other hand, while studying the infrared absorption spectra of solutions of organic compounds containing OH group in carbon tetrachloride observed that the solution of phenol shows a single absorption peak at 7050 cm^{-1} while *o*-chlorophenol gives two peaks at 6910 cm^{-1} and 7050 cm^{-1} respectively, the former being much stronger than the latter. These peaks correspond to the first harmonic of the fundamental O–H frequency 3520 cm^{-1}, and this difference between the behaviour of *o*-chlorophenol and that of phenol was first explained by Pauling (1936) who pointed out that in the solution of *o*-chlorophenol there might be two types of molecules, one having the OH group in the cis position and the other in the trans position with respect to the chlorine atom. Errera and Mollet (1935) also studied the infrared abosrption spectrum of pure *o*-chlorophenol in the region 1.3μ–1.8μ and observed a peak at 6620 cm^{-1} in place of the two peaks due to the solution in carbon tetrachloride mentioned above. The Raman spectrum of solution of *o*-chlorophenol in carbon tetrachloride was later

studied by Batuev (1945) who observed the OH line to be at 3533 cm^{-1} in the Raman spectrum of the pure liquid and the solution also yielded only a single line at 3540 cm^{-1}. Recently, Biswas (1954) studied the Raman spectra of o-chlorophenol in the liquid and solid states and observed that the line 3533 cm^{-1} due to O–H valence oscillation persists even when the crystals of the compound are cooled to −180°C. The results reported by Batuev (1945) do not indicate that the frequency of the O–H valence oscillation diminishes when the liquid is dissolved in carbon tetrachloride and are therefore contradictory to those on the infrared absorption in the region of 7000 cm^{-1} reported by previous workers It was, therefore, thought worthwhile to study the Raman spectra of solutions of o-chlorophenol in different solvents more carefully and to compare the intensity of the line 3533 cm^{-1} due to the pure liquid with that of the corresponding line due to the solution in order to find out whether any change either in the frequency or in the intensity of the line occurs when the liquid is dissolved in simple organic liquids. The present paper deals with these results

EXPERIMENTAL

The solvents used for the study of the Raman spectra of the solutions were carbon tetrachloride, chloroform and cyclohexane, the last one being chosen to avoid halogen atoms in the solvent molecules Ortho-chlorophenol of laboratory reagent quality was purchased from City Chemical Corporation of New York All the liquids were distilled under reduced pressure, as usual, and the Raman spectra of 15% and 30% solutions were photographed using a Fuess spectrograph having a dispersion of about 11·5 Å/mm in the 4046 Å region As the line 3533 cm^{-1} is very weak the spectra were photographed with long exposures to bring out this line clearly The spectrum was also photographed with the 4046 Å group of Hg lines cut off with rhodamine 6 GBM filter in order to assign the lines correctly. As preliminary investigations indicated that the intensity of the line 3533 cm^{-1} changes when the liquid is dissolved in the solvents mentioned above attempt was made to estimate the relative intensities of certain lines using blackening-log-intensity curves which were drawn with the help of microphotometric records of the continuous spectra of light from a tungsten filament lamp recorded with different known widths of the slit of the spectrograph As the line 3533 cm^{-1} is weak the background intensity had to be subtracted from the total intensity in order to derive the actual intensity of the line Microphotometric records of the spectra were obtained with the help of a Kipp and Zonen type recording microphotometer

RESULTS AND DISCUSSION

Some of the spectrograms are reproduced in figure 1, Plate V and some of the microphotometric records are reproduced in figure 2. It can be seen from

the latter figure that the line 3533 cm^{-1} excited by the 4046 Å line is weak and broad in comparison with a weak line at 1416 cm^{-1} excited by 4358 Å line in the spectrum due to the pure liquid, but in the spectra due to the solutions the line 3533 cm^{-1} is much stronger than the 1416 cm^{-1} line. The ratio of the intensity of the line 3533 cm^{-1} to that of the line 1416 cm^{-1} observed in the spectra due to the pure liquid and the solutions in carbon tetrachloride and chloroform are given in Table I. This ratio could not be determined in the case of the solution in cyclohexane, but in this case the Raman frequency of the line seems to increase to about 3550 cm^{-1}.

TABLE I

Ratio of intensities of the lines 3533 cm^{-1} and 1416 cm^{-1}

Substance	I_{3533}/I_{1411}
o-Chlorophenol pure	0.8470
30% solution in CCl_4	1.55
15% solution in CCl_4	1.88
30% solution in $CHCl_3$	1.47
15% solution in $CHCl_3$	1.62

Figure 1(a) shows that there is no line of Raman frequency slightly lower than 3533 cm^{-1} in the spectrum due to the pure liquid. The infrared spectra of the pure liquid in the region between 6000 cm^{-1} and 7200 cm^{-1} studied by Errera and Mollet (1935) and of the solution in carbon tetrachloride studied by Wulf *et al* (1935) show that in the case of the pure liquid there is a strong and broad absorption peak at about 6620 cm^{-1} with the indication of weak absorption at about 7050 cm^{-1}, and in the case of the solution there are two absorption peaks at 6910 cm^{-1} and 7050 cm^{-1} respectively, the former being nine times as large as the latter. These peaks are assumed to be due to harmonics of the O–H valence oscillations and the peak at 6910 cm^{-1} due to the solution was assigned by Pauling (1935) to the harmonic of the oscillations in O–H group in the cis position of the molecule with respect to the chlorine atom and the line 7050 cm^{-1} to the harmonic of such oscillations in the O–H group in the trans position. Similarly, the peak 6620 cm^{-1} given by the pure liquid was attributed to the harmonic of the oscillation in O–H group in the cis position with the oxygen atom of the O–H group forming a hydrogen bond with the hydrogen atom of the O–H group of a neighbouring molecule. It is, however, surprising that the Raman spectrum of the pure liquid does not show, besides the line at 3533 cm^{-1}, another line at 3310 cm^{-1} which would be the fundamental frequency corresponding to the harmonic at 6620 cm^{-1}. Similarly, the Raman spectrum due to the solution in carbon tetrachloride does not show a strong line at 3455 cm^{-1}

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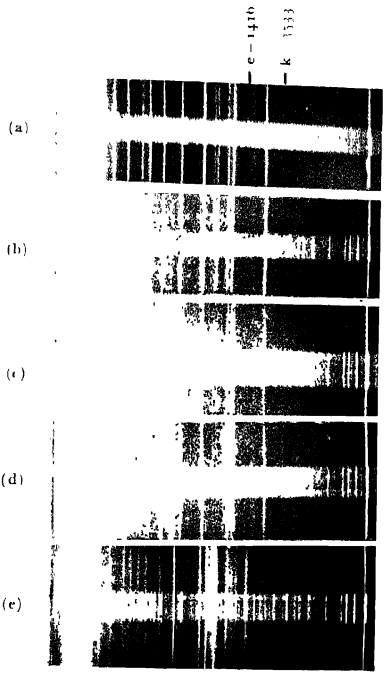
PLATE V



Raman spectra of ortho-chlorophenol

(a) Pure liquid
(b) ,, ,, excited with 4046 A. U. cut off
(c) 15% solution in CCl_4
(d) 30% solution in $CHCl_3$
(e) 15% solution in cyclohexane

as the fundamental of the harmonic at 6910 cm^{-1} observed in the infrared spectra. These facts seem to be anomalous.

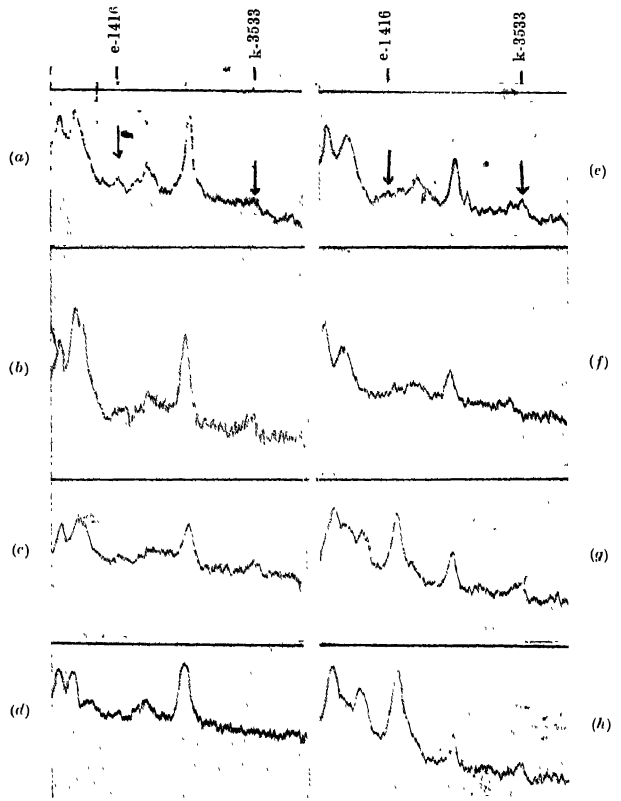


Fig. 1. Microphotometric records of Raman spectra.

(*a*) Pure *o*-chlorophenol in liquid state
(*b*) 30% solution in CCl_4
(*c*) 15% „ „ „
(*d*) Pure *o*-chlorophenol excited with 4046 A.U. group cut off.
(*e*) 30% solution in $CHCl_3$
(*f*) 15% „ $CHCl_3$
(*g*) 30% „ in cyclohexane
(*h*) 15% „ „ „

It is evident from the above facts that probably it is necessary to find out an alternative interpretation of these infrared absorption bands. As the Raman spectrum of the pure *o*-chlorophenol shows a faint line at 3533 cm^{-1} this line is to be assigned to the valence oscillation in the OH group which is not attached to the chlorine atom, as in the phenol molecule. This line is produced evidently by only a very small percentage of molecules in the pure liquid The corresponding oscillation in the cis position of the O–H group may have almost the same frequency, but probably the O–H vibration in this case cannot be excited without exciting simultaneously the C–H valence oscillation of the molecule Hence we expect to observe a combination line of Raman shift about 6600 cm^{-1} and the corresponding band was actually observed by Errera and Mollet (1935) in the infrared region The band at 1·51μ observed by them is probably not due to the harmonic of O–H valence oscillation, but it may be due to the combinational mode mentioned above. There is, however, a little absorption in the region 7050 cm^{-1} in the curve reproduced by Errera and Mollet, and this absorption may be due to the harmonic of the line 3533 cm^{-1} excited in a very small percentage of the molecules, as observed in the Raman spectrum of the pure liquid.

This alternative interpretation of the infrared bands of the pure liquid is offered, because the structure of the dimer which is assumed to be present in the pure liquid by Pauling (1935) indicates the presence of two types of O H groups, but in the Raman spectrum only one line due to O–H valence oscillation is observed Also, the formation of the hydrogen bond between the two molecules is expected to produce a shift in the electronic energy level with the change from the vapour to the liquid phase of the substance The ultraviolet absorption spectra of the vapour and the liquid were compared by Swamy (1953) but no appreciable shift was observed to take place with liquefaction of the vapour although large shifts were observed to take place with this change of state in the case of parachlorophenol This shows that such a change in the electronic energy level is produced by the chlorine atom the influence of which is diminished by the attachment of the hydrogen atom of the O–H group to it

As indicated in Table I the Raman spectra of the solutions show that the intensity of the line 3533 cm^{-1} increases when the liquid is dissolved in the solvents and it increases further when the concentration is diminished from 30% to 15%. As this line is to be assigned to O–H vibration in the molecule with the O–H group in the trans position the number of such molecules increases with lowering of concentration of the solutions. It is, therefore, quite unlikely that at a concentration of 01 molal 90% of the molecules in the solution in carbon tetrachloride may have the OH group in the cis position. The strong peak at 6910 cm^{-1} observed by Wulf *et al* (1935) is due to a 01 molal solution in carbon tetrachloride and the interpretation that 90% of the molecules in the solution have

the O-H group in the cis position and that these molecules produce this peak at 6910 cm^{-1} has probably to be revised in view of the results given in Table I. It has to be assumed now that at 01 molal concentration of the solution in carbon tetrachloride studied by Wulf *et al* (1935) almost all the *o*-chlorophenol molecules have the O–H group in the trans position It is, however, quite probable that this conversion from the cis to the trans form is caused by the chlorine atoms of the carbon tetrachloride molecule to which the hydrogen atom of the O–H group in most of the *o*-chlorophenol molecules may be loosely attached. Such an attachment is expected to diminish the frequency of the O-H valence oscillation, and this explains the diminution of the frequency of the harmonic from 7050 cm^{-1} to 6910 cm^{-1}. The weak peak at 7050 cm^{-1} is probably produced by the small percentage of molecules in which the hydrogen atom of the O-H group is not attached to the neighbouring carbon tetrachloride molecules. The lowest concentration of the solutions of which the Raman spectra have been studied in the present investigation is 15%. Even at this concentration the Raman line due to the O–H oscillation is very weak and therefore the majority of the molecules have the O–H group in the cis position. At this concentration probably the O–H group in the trans position in the remaining few molecules are not attached to the neighbouring carbon tetrachloride molecules owing to the influence of the *o*-chlorophenol molecules with the O–H group in the cis position which are still predominant in the solution at such a concentration.

In the case of the solution in cyclohexane such a diminution in the O-H frequency owing to the influence of the molecules of the solvent is not expected and it would be interesting to study the infrared spectrum of the solution in the region from 1·5μ to 1·7μ. The fact that the O–H frequency increases slightly in this solution shows that even in the pure liquid the intermolecular field slightly lowers the frequency of this vibration

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